organic papers

5-Fluorouracil–dimethyl sulfoxide (1/1)

Ashley T. Hulme* and Derek A. Tocher

Christopher Ingold Laboratory, Department of Chemistry, 20 Gordon Street, London WC1H 0AJ, England

Correspondence e-mail: a.hulme@ucl.ac.uk

Key indicators

Single-crystal X-ray study
$T = 150$ K
Mean σ(C–C) = 0.002 Å
Disorder in main residue
R factor = 0.036
wR factor = 0.090
Data-to-parameter ratio = 15.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_4H_3FN_2O_2 \cdot C_2H_6OS$, crystallizes in the monoclinic space group $P2_1/c$, with one molecule of 5-fluorouracil and one molecule of dimethyl sulfoxide (DMSO) in the asymmetric unit. The crystal structure contains hydrogen-bonded ribbons of alternating 5-fluorouracil and DMSO molecules which stack, forming non-interacting layers parallel to the (100) planes.

Comment

In the course of a polymorph screen performed on 5-fluorouracil three solvates were discovered; the crystal structure of one of these solvates is reported here. The title compound, (I), crystallizes in the space group $P2_1/c$ with one molecule of 5-fluorouracil and one molecule of dimethyl sulfoxide (DMSO) in the asymmetric unit.

(I)

The S atom in the DMSO molecule is disordered over two sites, with a 95:5 occupancy ratio. The minor site (S20′) exhibits the opposite pyrimidisation of the DMSO molecule, compared to the major site (S20). Fig. 1 shows the asymmetric unit, with only the major sulfur position shown.
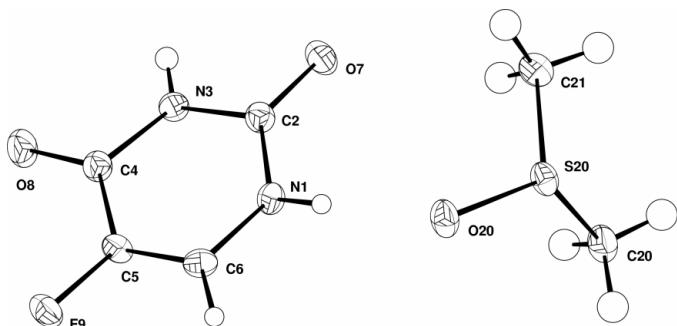
Figure 1
View (Watkin *et al.*, 1996) of the asymmetric unit of the title compound, with 50% probability displacement ellipsoids. H atoms are drawn as spheres of arbitrary radii.

Two conventional hydrogen bonds, of the type $N-H\cdots O$, occur in the structure. The O atom of the DMSO molecule acts as a hydrogen-bond acceptor for two symmetry-related 5-fluorouracil molecules (Table 1).

The crystal structure contains hydrogen-bonded ribbons of alternating 5-fluorouracil and DMSO molecules (Fig. 2). These ribbons stack, forming form non-interacting layers parallel to the (100) planes.

Experimental

5-Fluorouracil was obtained from the Aldrich Chemical Company Inc. The crystals of the title compound were grown by vapour diffusion of diethyl ether into a saturated solution of 5-fluorouracil in DMSO.

Crystal data

$C_4H_3FN_2O_2 \cdot C_2H_6OS$	$D_x = 1.562$ Mg m^{-3}
$M_r = 208.21$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 3031
$a = 9.8831$ (10) Å	reflections
$b = 10.8128$ (11) Å	$\theta = 2.9$–$28.0°$
$c = 8.6842$ (9) Å	$\mu = 0.36$ mm^{-1}
$\beta = 107.397$ (2)$°$	$T = 150$ (2) K
$V = 885.58$ (16) Å^3	Block, colourless
$Z = 4$	$0.29 \times 0.21 \times 0.11$ mm

Data collection

Bruker SMART APEX diffractometer	2128 independent reflections
Narrow-frame ω scans	1922 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$R_{int} = 0.022$
	$\theta_{max} = 28.3°$
$T_{min} = 0.903$, $T_{max} = 0.962$	$h = -13 \rightarrow 12$
	$k = -14 \rightarrow 14$
7672 measured reflections	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0401P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.036$	$+ 0.5099P]$
$wR(F^2) = 0.090$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
2127 reflections	$\Delta\rho_{max} = 0.40$ e Å^{-3}
140 parameters	$\Delta\rho_{min} = -0.54$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1$\cdots$O20	0.79 (2)	2.04 (2)	2.838 (2)	175 (2)
N3—H3$\cdots$O20^i	0.82 (2)	1.97 (2)	2.790 (2)	173 (2)
N1—H1$\cdots$S20$'$	0.79 (2)	2.56 (2)	3.266 (8)	149 (2)
N3—H3$\cdots$S20^i	0.82 (2)	2.89 (2)	3.666 (1)	157 (2)

Symmetry code: (i) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$.

The S atom in the DMSO molecule is disordered over two sites and was modelled anisotropically, with site occupancy 95:5. The S—O and S—C distances in the major and minor components were restrained to be equal within ±0.01 Å. All H atoms on 5-fluorouracil were located in a difference map and were refined isotropically; N—H = 0.79 (2) and 0.82 (2) Å, and C—H = 0.94 (2) Å. The H-atom positions on the methyl group were idealized and refined using a riding model [C—H = 0.96 Å and U_{iso}(H) = $1.5U_{eq}$(C)].
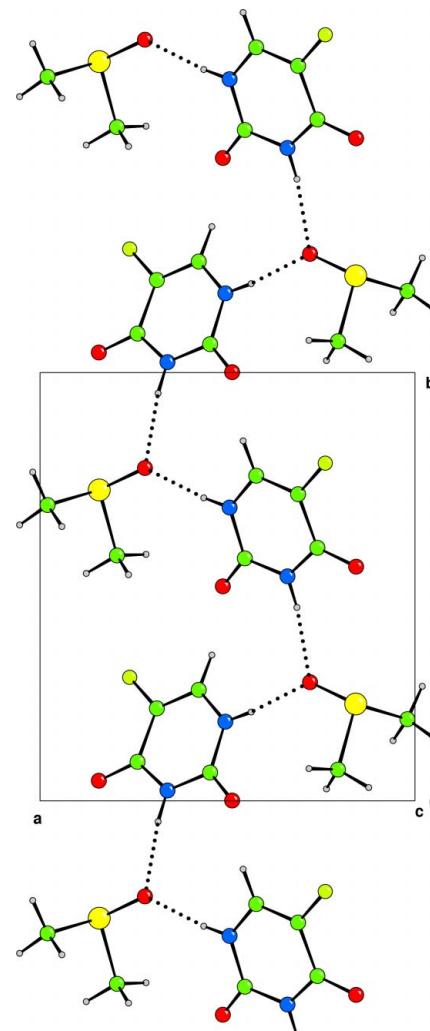
Figure 2
Hydrogen-bonded ribbon motif, made up of alternating 5-fluorouracil and DMSO molecules. Hydrogen bonds are shown as dashed lines.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *SHELXL*97.

References

Bruker (1998). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, Oxford, England.

5-Fluorouracil–dimethyl sulfoxide (1/1)

Ashley T. Hulme and Derek A. Tocher

5-Fluorouracil Dimethylsulfoxide (1/1)

Crystal data
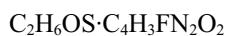
$C_2H_6OS \cdot C_4H_3FN_2O_2$	$F(000) = 432$
$M_r = 208.21$	$D_x = 1.562$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 3031 reflections
$a = 9.8831 (10)$ Å	$\theta = 2.9–28.0°$
$b = 10.8128 (11)$ Å	$\mu = 0.36$ mm^{-1}
$c = 8.6842 (9)$ Å	$T = 150$ K
$\beta = 107.397 (2)°$	Block, colourless
$V = 885.58 (16)$ Å^3	$0.29 \times 0.21 \times 0.11$ mm
$Z = 4$	

Data collection

Bruker SMART APEX diffractometer	7672 measured reflections
Radiation source: sealed tube	2128 independent reflections
Graphite monochromator	1922 reflections with $I > 2\sigma(I)$
ω rotation with narrow frames scans	$R_{int} = 0.022$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$\theta_{max} = 28.3°$, $\theta_{min} = 2.2°$
	$h = -13 \rightarrow 12$
	$k = -14 \rightarrow 14$
$T_{min} = 0.903$, $T_{max} = 0.962$	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	Secondary atom site location: found from delta F
Least-squares matrix: full	Hydrogen site location: found from delta F
$R[F^2 > 2\sigma(F^2)] = 0.036$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.090$	
$S = 1.07$	$w = 1/[\sigma^2(F_o^2) + (0.0401P)^2 + 0.5099P]$
2127 reflections	where $P = (F_o^2 + 2F_c^2)/3$
140 parameters	$(\Delta/\sigma)_{max} < 0.001$
7 restraints	$\Delta\rho_{max} = 0.40$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min} = -0.54$ e Å^{-3}

Special details

Experimental. The sulfur atom in the DMSO molecule is disordered and is modelled anisotropically, with site occupancy 95:5.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
S20	0.15779 (4)	0.27388 (4)	−0.05029 (5)	0.01947 (14)	0.9452 (19)
S20′	0.1956 (8)	0.3387 (7)	0.0775 (10)	0.047 (3)	0.0548 (19)
O20	0.27984 (12)	0.22286 (10)	0.08812 (14)	0.0242 (3)	
C20	0.02017 (18)	0.30934 (19)	0.0348 (2)	0.0310 (4)	
H20A	−0.0187	0.2340	0.0621	0.047*	0.9452 (19)
H20B	−0.0530	0.3549	−0.0420	0.047*	0.9452 (19)
H20C	0.0576	0.3583	0.1303	0.047*	0.9452 (19)
H20D	0.0033	0.2592	0.1184	0.047*	0.0548 (19)
H20E	−0.0138	0.2671	−0.0667	0.047*	0.0548 (19)
H20F	−0.0289	0.3867	0.0289	0.047*	0.0548 (19)
C21	0.20530 (19)	0.42683 (17)	−0.0857 (2)	0.0296 (4)	
H21A	0.2812	0.4246	−0.1335	0.044*	0.9452 (19)
H21B	0.2356	0.4710	0.0147	0.044*	0.9452 (19)
H21C	0.1249	0.4678	−0.1576	0.044*	0.9452 (19)
H21D	0.3041	0.4445	−0.0672	0.044*	0.0548 (19)
H21E	0.1541	0.5029	−0.0904	0.044*	0.0548 (19)
H21F	0.1691	0.3833	−0.1860	0.044*	0.0548 (19)
C6	0.57652 (17)	0.24074 (15)	0.4738 (2)	0.0203 (3)	
F9	0.76106 (11)	0.21144 (9)	0.71240 (12)	0.0274 (2)	
O7	0.48751 (13)	0.49901 (12)	0.21670 (14)	0.0288 (3)	
O8	0.84328 (13)	0.45295 (12)	0.68615 (15)	0.0300 (3)	
N1	0.50578 (15)	0.31511 (13)	0.34764 (17)	0.0202 (3)	
N3	0.66006 (14)	0.47552 (13)	0.45536 (16)	0.0195 (3)	
C2	0.54651 (16)	0.43374 (15)	0.33165 (18)	0.0194 (3)	
C4	0.73994 (16)	0.40891 (15)	0.58632 (19)	0.0197 (3)	
C5	0.68843 (17)	0.28387 (14)	0.58802 (19)	0.0199 (3)	
H1	0.439 (2)	0.2926 (18)	0.276 (2)	0.019 (5)*	
H3	0.685 (2)	0.548 (2)	0.448 (2)	0.027 (5)*	
H6	0.5414 (19)	0.1598 (18)	0.474 (2)	0.020 (5)*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S20	0.0212 (2)	0.0176 (2)	0.0164 (2)	0.00214 (15)	0.00069 (16)	−0.00209 (14)

S20′	0.066 (7)	0.043 (6)	0.032 (5)	0.012 (5)	0.014 (5)	−0.003 (4)
O20	0.0213 (6)	0.0183 (6)	0.0276 (6)	0.0039 (4)	−0.0006 (5)	−0.0006 (4)
C20	0.0207 (8)	0.0428 (11)	0.0277 (9)	0.0050 (7)	0.0044 (7)	0.0087 (8)
C21	0.0272 (9)	0.0267 (9)	0.0331 (10)	0.0027 (7)	0.0064 (7)	0.0094 (7)
C6	0.0245 (8)	0.0151 (7)	0.0226 (8)	−0.0018 (6)	0.0091 (7)	−0.0008 (6)
F9	0.0293 (5)	0.0233 (5)	0.0253 (5)	0.0022 (4)	0.0017 (4)	0.0084 (4)
O7	0.0295 (6)	0.0268 (6)	0.0237 (6)	−0.0024 (5)	−0.0019 (5)	0.0068 (5)
O8	0.0273 (6)	0.0261 (6)	0.0280 (7)	−0.0053 (5)	−0.0048 (5)	0.0013 (5)
N1	0.0190 (7)	0.0211 (7)	0.0173 (7)	−0.0046 (5)	0.0007 (5)	−0.0029 (5)
N3	0.0211 (7)	0.0140 (6)	0.0212 (7)	−0.0032 (5)	0.0029 (5)	−0.0001 (5)
C2	0.0195 (7)	0.0206 (7)	0.0176 (7)	−0.0001 (6)	0.0050 (6)	−0.0008 (6)
C4	0.0194 (7)	0.0199 (7)	0.0190 (7)	−0.0005 (6)	0.0043 (6)	−0.0004 (6)
C5	0.0223 (7)	0.0180 (7)	0.0188 (7)	0.0020 (6)	0.0050 (6)	0.0033 (6)

Geometric parameters (Å, º)

S20—O20	1.5288 (12)	C21—H21D	0.96
S20—C21	1.7710 (18)	C21—H21E	0.96
S20—C20	1.7729 (18)	C21—H21F	0.96
S20′—O20	1.492 (7)	C6—C5	1.330 (2)
S20′—C20	1.691 (7)	C6—N1	1.371 (2)
S20′—C21	1.734 (7)	C6—H6	0.94 (2)
C20—H20A	0.96	F9—C5	1.3534 (18)
C20—H20B	0.96	O7—C2	1.2192 (19)
C20—H20C	0.96	O8—C4	1.2215 (19)
C20—H20D	0.96	N1—C2	1.364 (2)
C20—H20E	0.96	N1—H1	0.79 (2)
C20—H20F	0.96	N3—C2	1.377 (2)
C21—H21A	0.96	N3—C4	1.378 (2)
C21—H21B	0.96	N3—H3	0.82 (2)
C21—H21C	0.96	C4—C5	1.446 (2)
O20—S20—C21	106.60 (8)	C2—N1—C6	122.53 (14)
O20—S20—C20	105.89 (8)	C2—N1—H1	114.2 (14)
C21—S20—C20	98.44 (9)	C6—N1—H1	123.3 (14)
O20—S20—H20E	126.7	C2—N3—C4	127.20 (14)
C21—S20—H20E	110.1	C2—N3—H3	116.1 (14)
O20—S20—H21F	126.7	C4—N3—H3	116.6 (14)
C20—S20—H21F	110.9	O7—C2—N1	122.98 (15)
H20E—S20—H21F	104.4	O7—C2—N3	121.84 (15)
O20—S20′—C20	111.9 (5)	N1—C2—N3	115.18 (14)
O20—S20′—C21	110.2 (4)	O8—C4—N3	122.22 (15)
C20—S20′—C21	103.2 (4)	O8—C4—C5	125.40 (15)
S20′—C20—H20C	66.5	N3—C4—C5	112.37 (13)
C5—C6—N1	120.15 (15)	C6—C5—F9	121.11 (14)
C5—C6—H6	123.3 (12)	C6—C5—C4	122.48 (14)
N1—C6—H6	116.6 (12)	F9—C5—C4	116.41 (14)

C5—C6—N1—C2	0.9 (2)	N1—C6—C5—F9	−179.01 (14)
C6—N1—C2—O7	177.16 (15)	N1—C6—C5—C4	0.5 (2)
C6—N1—C2—N3	−2.8 (2)	O8—C4—C5—C6	−178.74 (17)
C4—N3—C2—O7	−176.16 (16)	N3—C4—C5—C6	0.2 (2)
C4—N3—C2—N1	3.8 (2)	O8—C4—C5—F9	0.8 (2)
C2—N3—C4—O8	176.46 (16)	N3—C4—C5—F9	179.76 (13)
C2—N3—C4—C5	−2.5 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O20	0.79 (2)	2.04 (2)	2.838 (2)	175 (2)
N3—H3···O20[i]	0.82 (2)	1.97 (2)	2.790 (2)	173 (2)
N1—H1···S20′	0.79 (2)	2.56 (2)	3.266 (8)	149 (2)
N3—H3···S20[i]	0.82 (2)	2.89 (2)	3.666 (1)	157 (2)

Symmetry code: (i) −*x*+1, *y*+1/2, −*z*+1/2.